THE FORMATION OF NUCLEOBASES FROM THE UV IRRADIATION OF ASTROPHYSICAL ICE ANALOGS. C. K. Materese<sup>1,2</sup>, M. Nuevo<sup>1,2</sup>, and S. A. Sandford<sup>1</sup>, <sup>1</sup>NASA Ames Research Center, Moffett Field, CA, USA, <sup>2</sup>BAER Institute, Petaluma, CA, USA

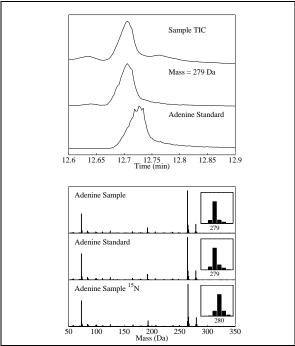
**Introduction:** Nucleobases are the fundamental information bearing components of both RNA and DNA. They are central to all known terrestrial life and they are generally conserved between species. Biological nucleobases can be divided into two groups based on the *N*-heterocyclic molecules pyrimidine (uracil, cytosine, and thymine) and purine (adenine and guanine) respectively. Do date, no experimental conditions have been determined that could produce both pyrimidines and purines together, abiotically, in a terrestrial environment or an early terrestrial analog.

Organic materials produced in extraterrestrial environments may have been delivered to the primitive earth by comets and meteorites and may have contributed to the emergence of life [1]. To date, some, but not all nucleobases have been detected in meteorites [2-4] and their isotopic signatures may be consistent with an extraterrestrial origin [5]. Earlier work in our lab demonstrated that it is possible to produce all of the pyrimidine group nucleobases from the UV-irradiation of pyrimidine in astrophysically relevant ice analogs [6-9]. Here we report our most recent work, which studied the formation of the purine group nucleobases under similar conditions [10].

**Experimental:** Gas mixtures of H<sub>2</sub>O and/or NH<sub>2</sub> were premixed in ~2L bulbs. Because of its low volatility, purine was prepared separately in an evacuated sample tube that was attached directly to the vacuum chamber, and wrapped with heat tape and a thermocouple to control and monitor the temperature and deposition rate. The gas/purine deposition rates were calibrated to establish a mixing ratio of 1.0:0.1:10<sup>-3</sup> for 3 component H<sub>2</sub>O:NH<sub>3</sub>:purine ices or 1.0:10<sup>-3</sup> for 2 component H<sub>2</sub>O:purine or NH<sub>3</sub>:purine ices. Throughout the deposition, the ice mixtures were simultaneously irradiated with an H<sub>2</sub>-discharge lamp emitting UV photons (Lyman α at 121.6 nm and a continuum at ~160 nm). After irradiation, samples are warmed to room temperature, and refractory residues are recovered for derivatization and analysis using gas chromatography coupled with mass spectroscopy.

**Results:** The UV irradiation of our ice mixtures resulted in the formation of refractory residues containing numerous functionalized purines. This included the nucleobases adenine (shown in the figure) and guanine, in addition to hypoxanthine, isoguanine, several aminopurines, and 2,6-diaminopurine. Overall, in both the most recent work, and in previous work, the relative abundance of photoproducts seems to be controlled by three factors in roughly decreasing order of

importance: 1) the number of functional group additions required to form the product; 2) the type of functional group added; and 3) the position where the addition takes place. Finally, our results demonstrate that all biological nucleobases can be produced under the same astrophysical conditions.



**Top panel:** (Top trace) Total-ion chromatogram (TIC) of the residue produced from a UV-irradiated H<sub>2</sub>O:NH<sub>3</sub>:purine ice. (Middle trace) Single-ion chromatogram (SIC) of the same residue for mass 279 Da. (Bottom trace) SIC of the adenine standard (mass 279 Da). **Bottom panel:** (Top trace) Mass spectrum of the peak identified as adenine in the residue produced from a UV-irradiated H<sub>2</sub>O:NH<sub>3</sub>:purine ice. (Middle trace) Mass spectrum of the adenine standard. (Bottom trace) Mass spectrum of the peak identified as adenine in the residue produced from an irradiated ice containing <sup>15</sup>NH<sub>3</sub>.

References: [1] Chyba C. and Sagan C. (1992) *Nature*, 355, 125. [2] van der Velden W. and Schwartz A. (1977) *Geochim. Cosmochim. Acta*, 41, 961. [3] Stoks P. and Schwartz A. (1979) *Nature*, 282, 709. [4] Callahan M. P et al. (2011) *Proc. Nat. Acad. Sci.*, 108, 13995. [5] Martins Z. et al. (2008) *Earth Planet. Sci. Lett.*, 270, 130. [6] Nuevo M. et al. (2009) *Astrobiology*, 9, 683. [7] Nuevo M. et al. (2012) *Astrobiology*, 12, 295. [8] Materese C. K. et al. (2013) *Astrobiology*, 13, 948. [9] Nuevo M. et al. (2014) ApJ, 793, 125. [10] Materese C. K. et al. (2017) *Astrobiology*, submitted.